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Transformation of Active Carbon to Onion-like Fullerenes Under Electron Beam Irradiation

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ABSTRACT

The transformation of an active carbon film with Pt nanoparticles to onion-like fullerenes has been in-situ investigated by a high-resolution transmission electron microscope. It was found that the onion-like fullerenes/metals polycrystalline film was formed under electron irradiation. The formation process was consisted of three steps: first, the flakes of onion-like fullerenes were induced by Pt nanoparticles; second, the flakes grew into a few ellipsoidal graphite shell; and third, a gradual reorganization of the formation of quasi-spheroid graphite shells and the bond of Pt particles was took place. It was a composite film of onion-like fullerenes and metal particles. It is suggested that the transformation mechanism involves an irradiation of electron and a catalytic effect of Pt nanoparticles, while any temperature rise due to electron irradiation seems to be negligibly small.

INTRODUCTION

Since the discovery of fullerenes, their synthesis and characterization have attracted a great deal of interest in the scientific community. The fullerenes with different structure such as buckminsterfullerene[1,2], nanotubes[3], onion-like fullerenes[4], and metal-fullerenes[5] have been produced by laser vaporization, resistive heating, and arc discharge. For onion-like fullerenes (OLF), Iijima synthesized the onion structure carbon by arc discharge[4], Ugarte obtained OLF from polyhedral graphite and nanotubes by intense electron bombardment. Such OLF were usually formed from ordered structure carbons. Xu reported the transformation of an amorphous carbon film with metallic nanoparticles of Al, Au and Pt into giant onion-like fullerenes induced by electron beam irradiation in a high resolution transmission electron microscope [6-8]. They were the first experiments in which OLF were formed from an amorphous carbon film using an electron irradiation technique and metallic nanoparticle catalysts. Four kinds of onion-like fullerenes have been produced, such as signal-nuclei OLF, multiple-nuclei OLF, intercalation OLF with metal atoms inside its shells, and metallofullerene with metal atoms in its center.

Here, an experimental study is reported in which onion-like fullerenes/metals film was produced from active carbon by electron beam irradiation and Pt nanoparticle catalysts. The kinetics and mechanism of their formation were also discussed.

EXPERIMENTAL

Pt nanoparticls were prepared on amorphous carbon films by Ar^+ beam sputtering. The ion acceleration voltage was 2-4kV, with a beam current of 0.2-0.3 mA. The process was done under vacuum of 10^{-4} Pa. The size of Pt nanoparticles ranges from 1 to 6 nm in diameter. The thickness of amorphous carbon film was 20 to 25 nm. To study the transformation of active carbon to onion-like fullerenes, the Pt nanoparticles were covered with active carbon as shown in Fig.1. The thickness of film was increased to 40-50 nm.

These metal nanoparticles and active carbon film specimen were irradiated at an intensity in the range of 0.3-3.3 $\times 10^{20}$e/cm^{2}sec in a high resolution transmission electron microscope JEM-2010. The formation of onion-like fullerenes was investigated by *in-situ* observations. The vacuum was better than 10^{-5} Pa. HRTEM images were recorded with a low intensity electron beam in order to prevent electron damage and to produce good quality micrographs after the specimen were strongly irradiated.

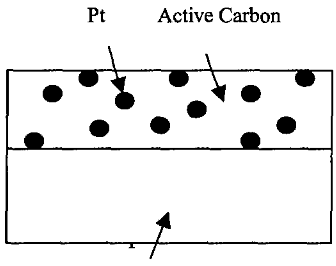

Fig.1 Schematic Diagram of HSTEM Specimen

RESULTS

Fig.2 shows an image of an active carbon film transformed into onion-like fullerenes, induced by 10% Pt nanoparticles under electron beam irradiation at an intensity of 3.3$\times 10^{20}$e/cm^{2}sec for 2800 sec. The nucleus of onion-like fullerenes was formed firstly in the area covered with active carbon. And it was achieved in the present of Pt nanoparticles. We also used an active carbon film without metal particles, and could not obtain onion-like fullerenes, even using the same experimental conditions.

The formation process of a composite film of onion-like fullerenes and metal particles was in-situ observed as Fig.3. The intensity of electron beam irradiation is 3.3$\times 10^{20}$e/cm^{2}sec. The process was divided into the following three steps. First, the nucleus and the first flake of a fullerene under the Pt nanoparticle are formed, which is indicated by the arrows in Fig.3(a). Second, the flakes grew into a few ordered structures as irregular ellipsoidal graphite shell with a large hollow interiors. It is showed in Fig.3(b). And third, a gradual reorganization of the formation of quasi-spheroid graphite shells and the bond of Pt particles was took place, as shown in Fig.3(c).

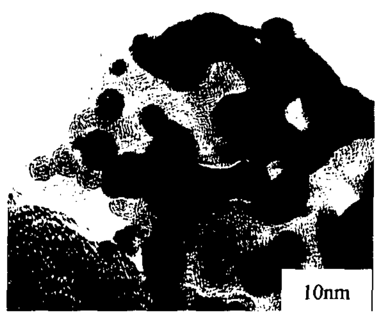

Fig.2 Onion-like fullerenes induced under 10% Pt nanoparticles by an electron irradiation at an intensity of 3.3 $\times 10^{20}$e/cm^{2}sec for 2800 sec

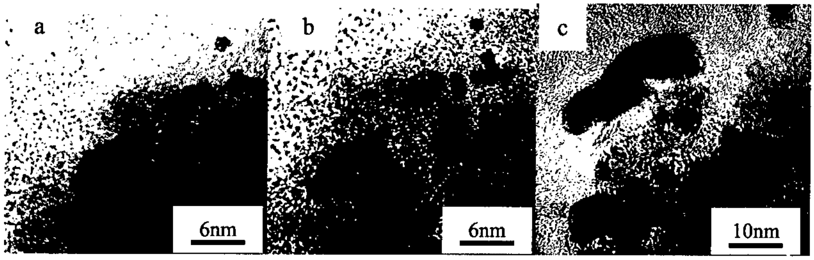

Fig.3 Onion-like fullerenes induced under 5% Pt nanoparticles by an electron irradiation at an intensity of 3.3×10^{20}e/cm^{2}sec for (a) 0 sec, (b) 1800 sec and (c) 3000 sec.

DISCUSSION

Nucleation of onion-like fullerenes

Fig.2 shows that the transformation of carbon to fullerene took place in the active carbon areas. Under the electron beam irradiation, the first elementary reaction is carbon atom catalyzed by Pt atoms on the surface of the nanoparticles to form a short range order C-C bond through rearrange from the active carbon. The catalytic effect of Pt atoms is also confirmed in Fig.3. It can be seen that all positions of the onion-like fullerenes cores correspond to the positions of Pt particles. It is clearly indicated that Pt atoms promote the formation of onion-like fullerenes. The nucleation sites are around the contact circle between Pt nanoparticles and the active carbon substrate, as confirmed by the fact that the larger fullerenes are induced around larger Pt particles.

Growth mechanism of onion-like fullerenes

As the the proceedings of the irradiation of electron beam, the C-C bond in a short range ordered structure changes into an ordered structure, such as a hexagonal or a pentagonal network, and finally forms the first flake of a fullerene by the self-diffusion of carbon atoms. The flakes grow into an ellipsoidal structure. Successive electron irradiation induces multiple ellipsoidal graphitic shells that finally change into a quasi-spheroid shape. The ellipsoidal graphitic shells expand their bonds along the surfaces of Pt nanoparticles and wrap them, thereby encapsulate them. The shells change in shape into spheres, which finally build the multiple quasi-spheroid shells, i.e. onion-like fullerenes, by an inner epitaxy[4] which eliminates the inner hollow. The driving force of onion-like fullerenes growth has been discussed in terms of a free energy minimization theory[4], which accounts for the highly stable spheroidal shape of carbon clusters and the multiple shell structure, which is more energetically favorable than a single or tubular shell. This process occurs spontaneously, and both results in the elimination of the dangling bonds, and promotes onion-like fullerenes with a maximum of 54 shells, which corresponds to about 105 carbon atoms in our experiment.

Transformation Drive Force

In the high temperature process, as in the arc discharge method, the nucleus of onion structure of carbon could be formed from a liquid drop. But, in the electron beam irradiation process, the first question is how high the temperature rise is. Recently, Xu[8] used Fisher's model to estimate the temperature rise to result in about 10 degrees at most. It is suggested that the heating effect by the electron irradiation is not a major effect for onion-like fullerenes formation. Hence, the formation and growth of onion-like fullerenes from active carbon can be considered as the electron stimulation effect and the catalysis effect of metal atoms.

CONCLUSION

Under the electron beam irradiation, the onion-like fullerenes can be transformed from active carbon film. The formation process was consisted of three steps: first, the flakes of onion-like fullerenes were induced by Pt nanoparticles; second, the flakes grew into a few ellipsoidal graphite shell; and third, a gradual reorganization of the formation of quasi-spheroid graphite shells and the bond of Pt particles was took place. It was a composite film of onion-like fullerenes and metal particles.

The transformation mechanism involves the electron stimulation effect and the catalysis effect of metal atoms, while any temperature rise due to electron irradiation seems to be negligibly small.

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